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**DEGRADATION AND BIODEGRADABILITY ENHANCEMENT OF
CHLORAMPHENICOL AND AZITHROMYCIN IN AQUEOUS SOLUTION USING
HETEROGENEOUS CATALYTIC OZONATION IN THE PRESENCE OF MGO
NANOCRYSTALIN COMPARISON WITH SINGLE OZONATION**

Hossein Arfaeinia¹, Kiomars Sharafi^{2,3}, Sara Banafshehshah¹, Seyed Enayat Hashemi^{3*}

¹Department of Environmental Health Engineering, School of Public Health, Iran University of Medical Sciences, Tehran, Iran

²Department of Environmental Health Engineering, School of Public Health, Kermanshah University of Medical Sciences, Kermanshah, Iran

³Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

⁴Department of Environmental Health Engineering, School of Public Health, Boushehr University of Medical Sciences, Boushehr, Iran

Email: e.hashemi@bpums.ac.ir

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Abstract

The catalyzed ozonation of antibiotic solution in the presence of Mg Onanocrystal as a catalyst was studied in a pilot scale batch reactor. The effects of various variables such as pH (3–13), reaction time, MgO dosage (0–10 g/L), and initial antibiotic concentration (0–50 mg/L) on CAP and AZM removal were investigated, and the results were compared to non-catalyzed ozonation. The optimized pH and catalyst dosage were found to be 8.5 and 6 g/L, respectively. The complete removal of CAP was found in COP at this optimum condition for an antibiotic concentration of 50 mg/L at a reaction time as little as 6 min, while the time needed to achieve the similar removal at conventional ozonation was 30 min. Moreover, the catalyzed ozonation can significantly enhance the BOD5 /COD ratio from below 0.1 in untreated solution to 0.41 to 0.68 for treated solutions; therefore, antibiotic was transformed to biodegradable substances. Thus, the COP with MgOnanocrystals can be taken into account as an feasible and effective technique for pre-treating the antibiotic-laden solutions, allowing the final-purified of the effluent in a biological treatment plant.

Keywords: Antibiotics, Chloramphenicol, Azithromycin, Catalytic Ozonation and MgO/O₃

Introduction

Today, antibiotics are commonly used in veterinary and human medicine, and the continual input of antibiotics into the water resources pose a potential danger for aquatic and terrestrial organisms(1). Some of the undesirable effects

that caused by antibiotics include, genotoxicity, resistance of pathogenic bacteria and endocrine disorders(2).

However, the drugs may not be extremely toxic, they can have cumulative impacts on the metabolism of non-target organisms(3) and on ecosystems(4). Because of antibiotic's high molecular complexity and their effects, these pollutants usually cannot be eliminated efficiently by conventional wastewater treatment approaches (5 and 6). Therefore, a great deal of attempts is being made to figure out methods of removing or inactivating this category of pollutants in surface water or wastewater (7 and 8).

Some of these antibiotics, such as semi-synthetic azithromycin(AZM, Figure1.a) are wide range antimicrobial agents that are used for treatment of infectious disease in humans and animals(9). This antibiotic is acid-stable and penetrates more broadly into tissues. With human metabolism being ignorable, this erythromycin derivative is disposed largely without changing into bile and can eventually be determined in effluents and surface waters (10 and 11). It is reported that Azithromycin concentrations ranged from 4.4 ng/L to 52.6 ng/L in wastewater treatment plant samples from Murray, Kentucky, USA (Mowery HR 2010 12). Another antibiotic that receives extensive attention due to a wide usage all over the world is Chloramphenicol (CAP, Figure1.b). This antibiotic is effective versus Gram-negative and Gram-positive cocci and bacilli, which makes it a favorite option to treat human and animal diseases(13). In China, CAP was found in municipal wastewater, the Nanming River and the sediment of Nanming River of Guiyang City, at concentrations up to 47.4 µg/L, 19.0 µg/L and 1138 µg/kg(Liu et al. 2009 14). It is also reported that the detected concentrations of CAP sewage treatment plant effluents and river, in Germany were up to 0.56 and 0.06 µg/L, respectively (15). A review paper showed that many of antibiotics in wastewater treatment plant influent were just partially eliminated after the all treatment units despite the various biological treatment methods(16). One research in Dalian (China) has also showed that six wastewater treatment plant showed poor removal for seven antibiotics present in influents (17). Meantime, the under study antibiotics have been observed in different points of coastal waters close to the discharge outfalls of wastewater treatment plant effluents(18). Thus, limit the release of these emerging pollutants from wastewater treatment plants could be an efficient technique to diminishing their occurrence in the surface waters.

Further purification process, after the common biological steps, such as membrane technologies (19), adsorption processes(20), advanced oxidation processes (AOPs)(21) and the combination of mentioned process(22)have been suggested and evaluated to removal emerging pollutant in wastewater treatment plants. One of these purification process is Advanced Oxidation Processes (AOPs) that are able to degrade antibiotics and purify water(23). Moreover,

it has been demonstrated that the complete elimination of the pollutant to enhance biodegradability of the effluent is not necessary, showing that the by-products of AOPs that remained after treatment are biodegradable and so more suitable for biological degradation(24-26). Up to now, various AOPs have been studied and proposed for employ in the water and wastewater treatment plant, most of which are based on employing ozone as the main oxidant(27). Catalytic ozonation process (COP) is one of the novel AOPs which has drawn general attention due to its capability to improve the decomposing persistent organic pollutants without high reaction pressure and temperature and low adverse effect on water characteristics (28).

In fact, adding a catalyst to the ozonation process leads to an increased degradation rate and decreased process time, therefore reducing the treatment cost(29). The COP can be employed either homogeneously or heterogeneously(30 and 31), with each way degradation organic molecules by direct oxidation with ozone molecules and/or by indirect radical oxidation(32). Heterogeneous catalytic ozonation is a suitable wastewater treatment process because of its lack of secondary pollution, low cost, and potential for catalyst reclamation(33).

The choice of catalyst is critical for catalytic ozonation process. Metal oxides (MnO_2 , TiO_2 , Al_2O_3 , and so on), supported metals or metal oxides ($\text{Cu}/\text{Al}_2\text{O}_3$, Cu/TiO_2 , Ru/CeO_2 , Co/SiO_2 , $\text{TiO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{CoOx}/\text{Al}_2\text{O}_3$, and MnOx/ZrO_2), and some porous materials (GAC, zeolite, ceramic honeycomb, etc.) are the main proposed catalysts(34). Moreover, nanosized alkaline earth metal oxides are very promising materials for catalyst usage because of their high surface reactivity(35), destructive sorbence(36), adsorption capacity the simplicity of their production from abundant natural minerals(37) and large specific surface areas, and thus a large fraction of active sites are available for appropriate chemical interaction(38).

One study observed that using magnesium oxide (MgO) as a catalyst in with ozonation process could improve phenol and COD removal from aqueous solution(32). However, the catalyzing capabilities of MgO in the COP for antibiotic removal have not been reported.

This work focused on the preparation and application of MgO nanocrystals as catalysts in the COP, comparing the performance with ozonation alone in the removal of two antibiotics including chloramphenicol and azithromycin from aqueous solution.

The effect of the main operational variables, including pH, reaction time, catalyst dose, and initial antibiotic concentration, on the COP's performance will be compared to the performance of ozonation alone under the same conditions.

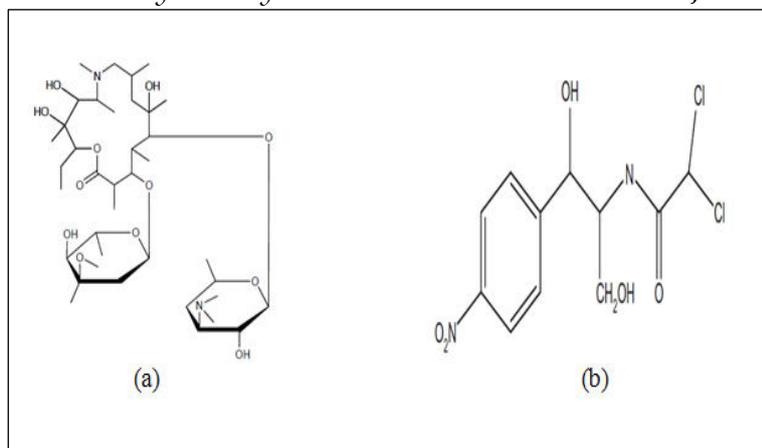


Figure-1. Chemical structure of AZM (a) and CAP (b)

Material and Methods

Solutions and chemicals

Azithromycin ($C_{38}H_{72}N_2O_{12}$) and Chloramphenicol ($C_{11}H_{12}Cl_2N_2O_5$) that used as the probe to investigate the catalytic ozonation process was obtained from Sigma Aldrich (St Louis, MO, USA). Acetonitrile (CH_3CN , HPLC grade) and methanol (CH_3OH , HPLC grade) were obtained from DyStar Co (Germany). $MgCl_2 \cdot 6H_2O$, tert-butanol (TBA), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were purchased from Merck Company (Darmstadt, Germany). Azithromycin and Chloramphenicol standard used for establishing standard curve was supplied by the Merck Company (Darmstadt, Germany). All chemicals were analytical grade. All other materials such as sodium potassium iodide, thiosulphate etc., were of reagent grades and were supplied from Merck, Germany. The pH value of the solution was adjusted by H_2SO_4 and NaOH.

• 2.2. Preparation of MgO nanoparticles

There are hydrothermal and sol-gel techniques for synthesizing the MgO nanoparticles. In this study, we applied the sol-gel method for nano-MgO synthesizing. To preparation of MgO nanoparticles, first 100 g of $MgCl_2 \cdot 6H_2O$ was dissolved in 500mL of distilled water in a 1-L bowl, then 50mL of 1N NaOH solution was added. After that, the solution was rapidly shaken and stirred for 4 h to produce the magnesium hydroxide precipitates.

The resulted suspension was centrifuged at 3500 rpm for 3 min to achieve the $Mg(OH)_2$ gel, thereafter, it was washed with distilled water for several times and hold to be dried at 65 °C for 24 h. Then, the dried powder was ultimately calcinated at air in 500 °C for 2 h and MgO nanoparticles were such composed.

• Ozonation and Catalytic ozonation protocol

Catalytic activity measurements in the degradation of chloramphenicol and azithromycin were carried out at room temperature (20-30°C) in a 1.3 L semi-batch cylindrical stirred reactor ($h=500mm$, $\phi_{in}=60mm$) made of stainless steel.

Ozon (0.5 g/hr output) was produced in situ from pure oxygen ($1.2\text{L}\cdot\text{min}^{-1}$) by a commercial generator (ARDA, model AEGCOG-5S) and fed to the solution through a stainless steel plate at the bottom of the reactor. The excess ozone in the off-gas stream was quenched and destructed by a KI solution. Various operational variables, including pH of the antibiotic solution, antibiotic concentrations, catalyst dose, and reaction time, were investigated. MgO nanocrystals were used as the ozonation catalyst for oxidation of the chloramphenicol and azithromycin. Moreover, control experiments with ozonation alone were conducted to verify the catalytic nature of the MgO nanocrystal. 2% KI solution was used to quench the continuous ozonation reaction in the samples.

- **Analytical procedures**

Procedures XRD measurements of the samples were carried out using X-ray diffraction (XRD) method (Philips diffractometer type XPERT). The surface morphology of the powders was analyzed using the scanning electron microscopy (SEM) technique (Philips-XL30 Electron Microscope). N_2 adsorption/desorption isotherms at 77 K by an Physisorption Analyzer (Micromeritics/Gemini-2372) were used to measuring the specific surface area, the pore volume and average pore diameter of the prepared nanocrystals. For performance evaluation of catalytic ozonation in degrading antibiotics and organic content that is related to these antibiotics, samples were taken at the beginning and end of the reaction from each experimental run. The high performance liquid chromatography (HPLC, CECIL, 4100) equipped with a UV detector (UV/VIS model 4200) at 230 nm. A C18 column ($5\ \mu\text{m}$, 250 mm long \times 4.6 mm ID) was used to determine antibiotics concentration. The mobile phase in these procedures was consisting of a mixture of acetonitrile and water (20/80, v/v). The flow rate was adjusted at $1.0\ \text{mL}\ \text{min}^{-1}$, and 20 μL of samples was injected in each injection. The pH value was measured with an electrode (Sense Ion 378, Hack). Standard method of potassium dichromate oxidation was used to COD measurement (Federation and Association 2005). Iodometric titration method were used for analyzing the ozone concentration in the inlet gas stream (39).

To make sure repeatability of data, each experiment was performed in duplicate and the mean of the two values was reported.

Result and discussion

- **Characterization of the catalysts**

As observed in Figure 2, XRD patterns of synthesized MgO shows the pure and cubic periclase MgO crystalline particles in this nanocrystals (36). Scherrer's equation (40) were used to determine the mean size of crystals, average size calculated from this equation was found to be 45 nm. Figure 3 shows the SEM image for the surface morphology

of the synthesized MgO nanocrystals, this image shows agglomerated, porous, and honey-combed nanocrystals.

According to this image, the size of MgO particles was determined to range among 23 and 53 nm, which is greater than that found by Nagappa and Chandrappa(36).

The nitrogen adsorption-desorption isotherm shown that the synthesized nanocrystal had a BET surface area of $137\text{m}^2/\text{g}$ and a total pore volume of 0.162cc/g and average size of the pores was found to be 4.7 nm. These results indicate that the powder that composed in this work was composed of mesoporous nanocrystals that had a high specific surface area.

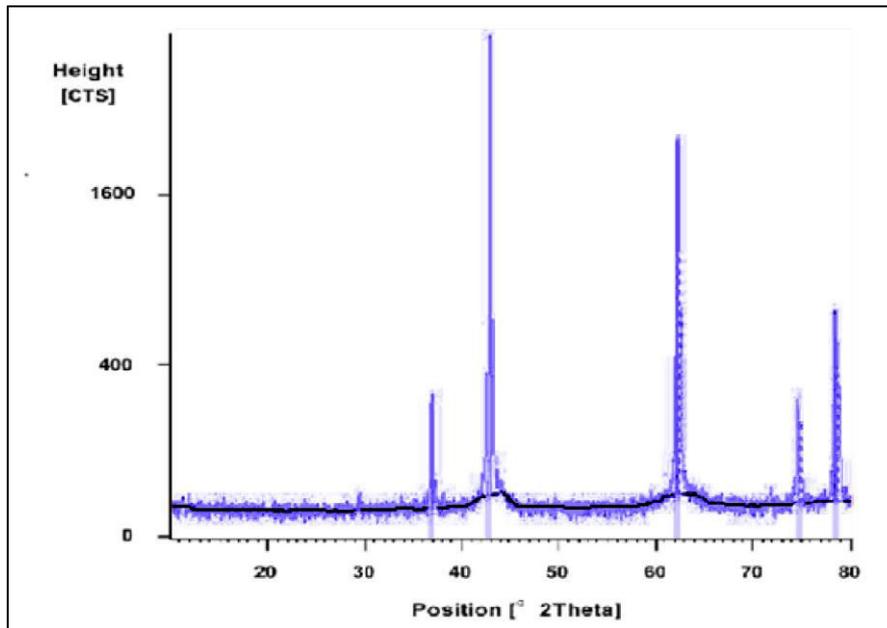


Figure- 2.XRD pattern of the MgO nanocrystals.

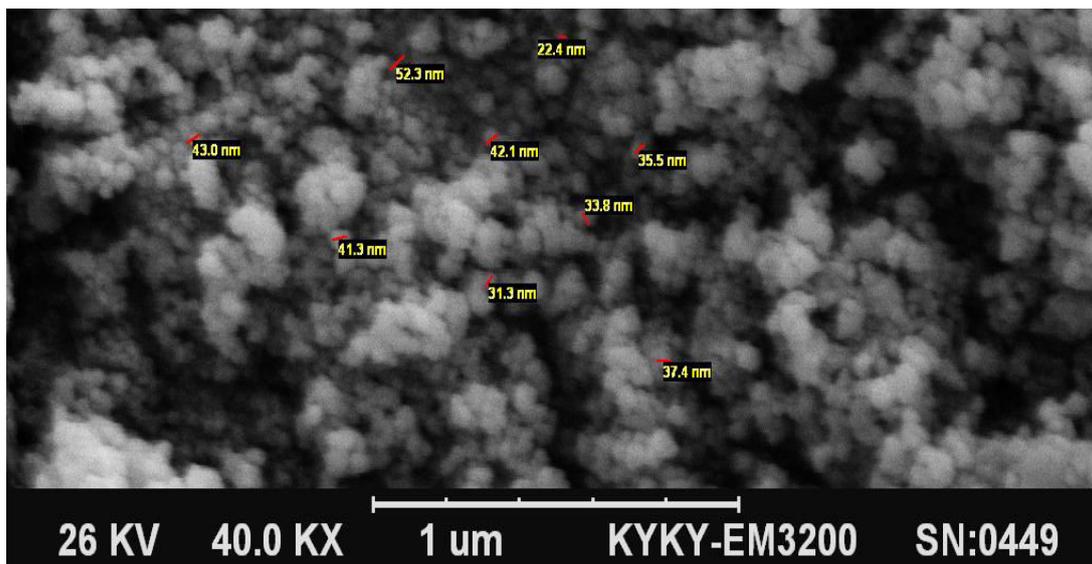


Figure-3.SEM image of the MgO nanocrystals.

- Mineralization of AZM and CAP by catalytic ozonation at different pH levels

There are two direct effects of pH on the oxidation, i.e. in a heterogeneous catalytic ozonation system. the first one is effect on ozone decomposition and the second one is effect on the surface property of solid catalyst(41). In a

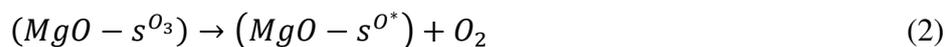
heterogeneous catalytic system, pH also can affect the surface property of metal oxides(42).Therefore, Since solution pH has an important role in the pollutant decomposition mechanism during an oxidation process, it is relevant to assess the effect of pH in catalytic ozonation of the selected model antibiotics from two perspectives including: a) Effect of pH on ozonation b) Effect of pH on MgO catalyzed ozonation.

The effect of the antibiotics solution's initial pHs on decomposition of antibiotics was studied in both catalytic ozonation and non-catalyzed ozonation with MgO nanocrystals at pH values of solution ranging between 3 to 13, under constant initial antibiotics concentration, ozone dosing and reaction time. Figure 3 indicates the removal percentages of AZM and CAP in different initial pH in non-catalytic and catalytic ozonation, respectively. As illustrated in Figure 3a the removal percentage of CAP in the non-catalytic ozonation at an acidic pH of 3 was 84%, and it diminished to 81% when pH was increased to 5. The high antibiotic removal at a pH of 3 is due to the direct oxidation of ozone with pollutant molecules, which is more performed at more acidic conditions(30). The removal of CAP from the samples increased for a pH above 5 and achieved highest amount of 93% at a pH around 10, which is 14% higher than that at a pH of 5. In alkaline conditions, due to an increase in ozone decomposition rate, the more reactive radicals are produced(43). Therefore, most of the degradation of these pollutants at alkaline conditions probably happens by indirect oxidation with reactive radicals. Nevertheless, some direct oxidation also might happen with non-decomposed ozone molecules. Minghao Sui et al.(34) pointed out greater ciprofloxacin removal efficiency by ozonation at alkaline conditions (pH 10.1) than acidic conditions (pH 3). They suggested that this result is due to ozone decomposition into hydroxyl radicals which appear to be responsible for high potential of oxidative activity at high pH. Fig.3a also shown the trend of AZM (as another target antibiotics in this study) removal as a function of the solution pHs. AZM Removal followed almost the same trend of CAP removal with the value of 81% at a pH of 10, where the highest CAP removal was found. As represented in Fig 3a, removal efficiency of AZM were lower than CAP removal in all pH values. The probable explanation for this phenomena could be higher benzene rings in AZM comparing to CAP.

Figure 3b illustrates the AZM and CAP removal by catalytic ozonation with MgO nanocrystals. It presents that a removal of 93 % CAP was achieved at a pH of 3, but the degradation decreased to 87% when the pH was lowered to 5. This indicates that the removal of CAP with catalytic ozonation in acidic condition was because of direct oxidation by the ozone molecules, like with non-catalyzed ozonation. The removal of CAP started to rise with the rise of pH above 5, achieving a maximum of 98% at a pH of 8.5. For AZM removal versus solution pH in the catalytic

ozonation process (Figure 3b), the findings showed a similar trend of CAP removal, but with a lower rate. AZM removal diminished from 84% at a pH of 3 to about 80 % at a pH of 5, and it then increased to 87% when the pH was increased to 8.5. However hydroxyl radicals are mostly built up at pHs above 10(44 and 32), but the highest CAP and AZM removal observed at pH of 8.5. This can be attributed to production of other radical species; also the MgO may have lowered the optimum pH for formation of hydroxyl radicals. The percentage of AZM removal remained almost constant with the increase of pH to 13. It is though that, in this alkaline pH, hydroxyl radicals are the dominant species predisposing higher degradation and consequently AZM removal. These results suggest that the pH of the solution has an important role in both non-catalyzed and catalytic ozonation of antibiotics, and that catalytic ozonation performed better in CAP and AZM removal in a much lower time.

The high percentage of CAP and AZM removal correlating with alkaline condition can be explained with the resulting enhance in available hydroxide ions and intensification of the ozone decomposition that as a result increases the generation of reactive radicals such as hydroxyl and MgO-hydroxyl radicals. It is assumed formation of radical in the presence of MgO as a catalyst and initiator for radical generation in the bulk solution in catalytic ozonation process is happened by following reactions: The action of MgO as a primer for radical generation and the decomposition of ozone on the surface of MgO are the main cause of active radical production.



(The suffix *s* in MgO-s indicates the Lewis acid site on the MgO surface).

As illustrated in Equations (1) to (3), various radicals are formed in this mechanisms, all leading to enhancement in antibiotic degradation. These formed radicals caused indirect oxidation of the antibiotic molecules with higher rates than those observed with solely ozone oxidation(45) and thereby improved the degradation of organics pollutant. Faria et al(46) proposed similar mechanisms for oxidation of sulfonated aromatic compounds in catalytic ozonation at the presence of activated carbon.

It is recognized that the ozonation of a solution with alkaline pH could leading to generation of high reactive radicals (32), mostly hydroxyl radicals. Figure 3 oobviously indicates this phenomenon for single ozonation of antibiotics. A comparison of single and catalytic ozonation with MgOnanocrystals (shown in Figure 3) shown that MgO can decrease the pH at which radicals generate in the ozonation process. It can be concluded that MgOnanocrystals

efficiently catalyzed the ozone decomposition and accelerated the production of reactive radicals, resulting in an enhanced degradation rate and therefore a decrease in the needed reaction time. These are crucial characteristic from both economical and operational viewpoints. However few authors(32 and 45) have formerly suggested that some metal oxides are good catalysts that caused decomposition of ozone into oxidative radicals, type of generated radical and the order of chemical reactions mainly depends on the reaction conditions and the type of metal oxide. Since the CAP and AZM removal in catalytic ozonation process was maximum at a pH of 8.5, this value was selected as the optimum pH in the subsequent steps of study.

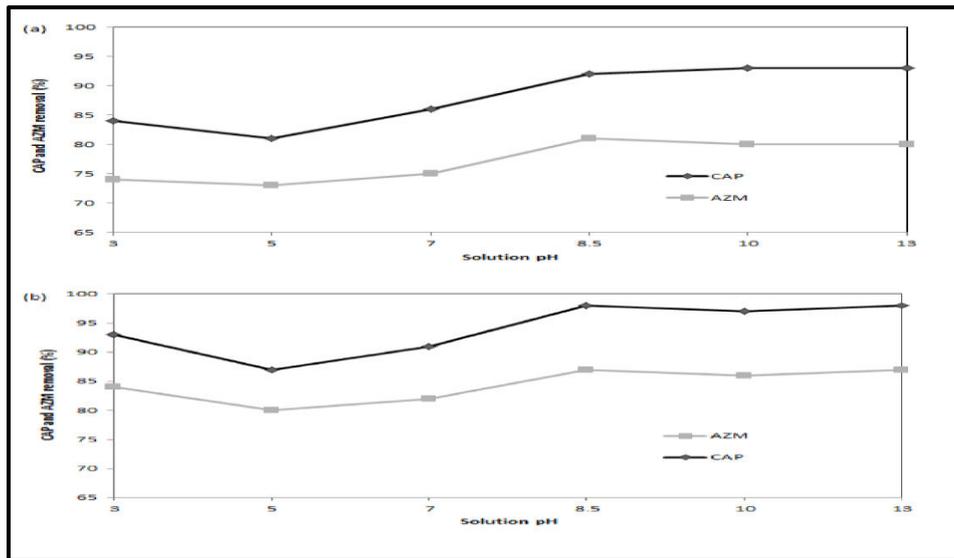


Figure-4. Effect of initial pH on CAP and AZM removal antibiotic solution in: (a) the conventional ozonation process((Initial concentration = 50 mg/L, reaction time = 25min), and (b) the COP (Initial concentration = 50 mg/L, MgO dosage = 6 g/L, reaction time = 10min).

• **Effects of variations in reaction time**

Another important factor influencing the design, operation and function of an ozonation process is the reaction time, which is the time needed to achieve favorable purposes of the treatment. On this basis, the second step of this research was to study the antibiotic removal by catalytic ozonation in different reaction times, under antibiotic concentration of 50 mg/l and optimum initial pH values of 8.5, compared with sigleozonation in similar conditions. Fig.4 illustrates the CAP and AZM removal against the reaction time under the determined conditions in single and catalyzed ozonation processes, respectively.

As shown fig.4, it could be seen that removal of both CAP and AZM enhanced with a raise in reaction time for both single and catalyzed process, however at a rate further for CAP than AZM removal, and further for catalyzed than single ozonation processes. For single ozonation process, the CAP removal enhanced from zero at the beginning of the process to about 47% after 5 min of ozonation (Figure 4a). Increasing the reaction time to 15 and 30 min led to

81% and 95% CAP removal, respectively. A similar result was found for AZM removal in the conventional ozonation. The AZM removal was 38 % after 5 min of ozonation, and it enhanced to 75% and 89% after 15 and 30 min, respectively (Fig. 4a). The findings show that the antibiotic degradation in single ozonation process follows a pseudo-first order reactions, with a reaction constant of about 0.17/min.

Figure 4b shows the finding of CAP and AZM removal in the catalytic ozonation with MgO nanocrystals as a catalyst. As seen, catalytic ozonation can attain 82% CAP removal after a reaction time of just 2 min. The percentage of CAP removal enhanced to 86% after 4 min and to 100% after 6 min of the reaction. Moreover,

The catalytic ozonation attained 95% removal of AZM from the solution after 6min of the reaction. Like to the single ozonation process, the degradation of antibiotic in the catalytic ozonation was shown to be a pseudo-first-order reaction with constant of 0.59/min. Comparing the findings shows that adding MgO nanocrystals to the reactor can considerably accelerate the degradation rate of antibiotic. Generally, the greater the rate of the ozonation reaction the lower the time needed to complete the reaction and, consequently, the shorter the needed reactor size and treatment cost.

No already published research can be found on catalytic ozonation of antibiotics using MgO for comparison with findings of this study. The results of this work show that MgO nanocrystals are very helpful catalysts for using in ozonation of antibiotic-containing wastewaters. Because of their destructive capability(47), high surface area and reactivity(48) and simplicity of their generation from plenty natural mineral such as brucite, MgO nanocrystals are promising catalysts from both economical and technical viewpoints for the reinforcement removal of organic pollutants from wastewaters.

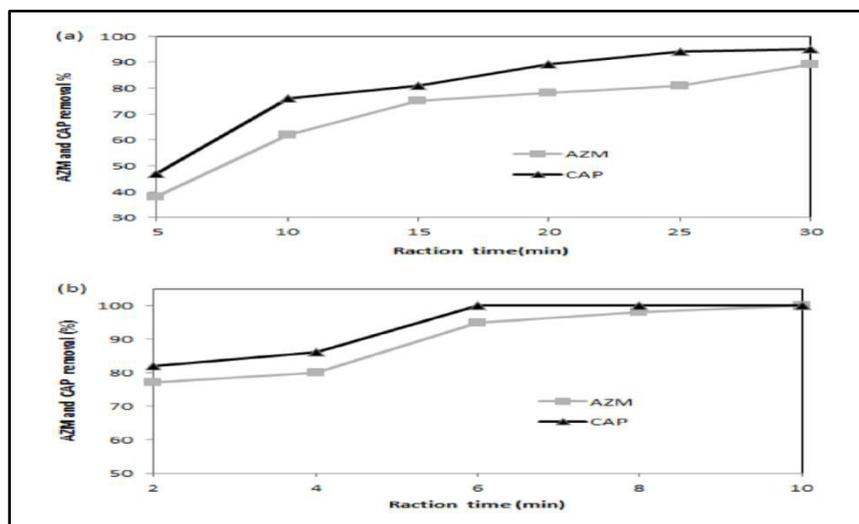


Figure-5. Effect of reaction time on CAP and AZM removal antibiotic solution in:
(a) the conventional ozonation process (Initial concentration = 50 mg/L, initial pH 8.5),
and (b) the COP (Initial concentration = 50 mg/L, MgO dosage = 6 g/L, initial pH 8.5).

- **Effects of variations in MgO dosage**

The catalyzed ozonation of antibiotic solution in the presence of different dose of MgO nanocrystals (ranging between 0 and 10 g/L) was investigated, and the relative performance in the decomposition and antibiotic removal turned out. All tests in this step were conducted at the constant reaction time of 6 min (at which the former steps indicated 100% CAP removal), at an antibiotic concentration of 50 mg/L, and at the optimum pH of 8.5. Figure 5 shows the CAP and AZM removal in different catalyst dose in the solution under reaction, revealing an enhancing impact of MgO as a catalyst in the ozonation process. As demonstrated in Figure 5, the CAP removal increased from 49% in the absence of catalyst to 85% in the presence of 2 g/L MgO powder. Thence, it enhanced slowly to over 99% when the MgO dosage was increased to 6 g/L. A further increase in MgO dosage to 10 g/L did not enhance the CAP removal. Therefore, relatively a low dosage of MgO is required to catalyze and improve the degradation of antibiotics. This can be attributed to the high surface area of MgO, which lets a little value of MgO to provide the needed reactive surface for the ozone entered to the reactor to stimulate and enhance the series of radical reactions. The removal of AZM indicated a similar trend with the dosage of MgO (Figure 5). As seen in Figure 5, removal of AZM enhanced almost linearly from 38% to 78% with the increase of MgO dosage from zero to 6 g/L at a constant contact time; further adding the catalyst dosage caused no substantially change in the removal of AZM. Since the CAP and AZM removal in catalyzed ozonation process was highest at 6 g/l, this value was selected as the optimum MgO dosage in the subsequent steps of study.

Moussavi et al.(35) reported that adding 5g/l of MgO powder to a red 198 azo dye solution in an ozonation reactor accelerated the oxidation efficiency. Likewise, other author have observed increased oxidation efficiency in metal-based catalyzed ozonation process with increased catalyst dosage (49). Nevertheless, the optimal catalyst dosage depends considerably on some factors such as the type of catalyst, the reactant(s), and the reaction conditions.

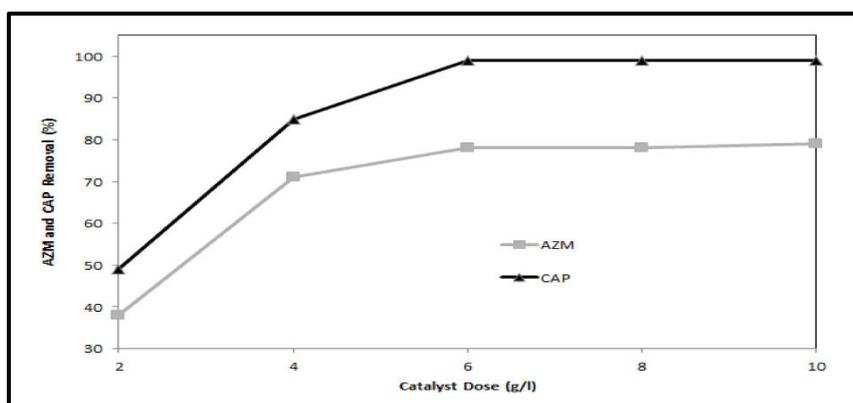


Figure-6. Effect of MgO dosage on CAP and AZM removal antibiotic solution in the COP (Initial concentration = 50 mg/L, initial pH 8.5, reaction time=6 min).

• Effects of variations in initial antibiotic concentration

However industrial wastewaters usually have different levels of antibiotics, many of the researches on catalytic ozonation have been performed using a specific target pollutant concentration. Thus, it is very critical from practical viewpoints to investigate how the initial antibiotic concentration influences the operation of a catalyzed ozonation in the removal of antibiotics and other organic pollutants. The effects of antibiotics concentrations of 0–50mg/L on CAP and AZM removal in the catalyzed ozonation was studied at an initial reaction time of 6 min and pH of 8.5. Figure 6 indicates the CAP and AZM removal at different initial concentrations.

As illustrated in Figure 6, the CAP removal percentages in catalyzed ozonation for initial levels of 5, 15, 25, 35 and 45mg/L were 100%, 98%, 93%, 90% and 86%, respectively, demonstrating a trend of lowered removal with increasing initial concentration. The AZM removal percentage for the corresponding antibiotic concentrations were 95%, 89%, 81%, 74% and 68%, respectively, indicating a similar diminution trend. The rate of diminution in AZM removal percentage was more than that for CAP, showing that more ozone is needed to oxidize the intermediates from the antibiotic decomposition. This could be provided by improving the ozonation dose either via increased ozonation time and/or increased ozone flow rate.

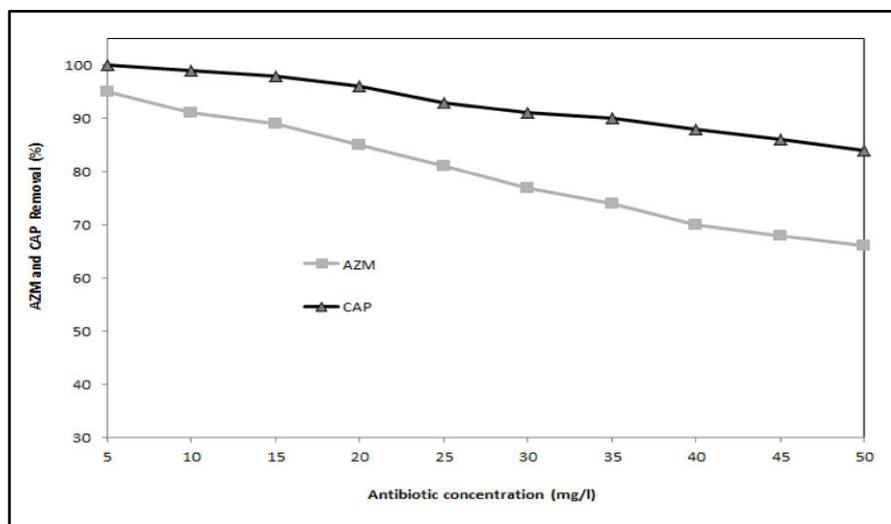


Figure-7. Effect of Initial concentration on CAP and AZM removal antibiotic solution in the COP (initial pH 8.5, reaction time=10 min, MgO dosage = 6 g/L).

Improvement in biodegradability of ozonation effluent

The BOD₅/COD ratio is usually used for evaluate the biodegradability of wastewaters and effluents(50). The biodegradability of untreated and ozonation-treated antibiotic effluents was studied at various levels to indicate the ability of biological treatment for the post-treatment of ozonation-treated effluents. The findings are displayed in Figure7. It is n

oteworthy that the ratio of BOD₅/COD in untreated solution at all antibiotic concentrations was under 0.1, showing that CAP and AZM are refractory pollutants. As illustrated in Figure 7, the BOD₅/COD ratio of the antibiotic solution at all target concentrations after pretreatment step in catalyzed ozonation (under condition of MgO dose = 6 g/L, pH 8.5 and reaction time = 6min) enhanced and ranged between 0.41 to 0.68. This results show that the biodegradability of antibiotic considerably enhanced with a little reaction time in catalyzed ozonation process and was turned into a biodegradable waste. The improvement of the biodegradability is corresponding to cleavage of the aromatic rings and therefore the conversion of the antibiotic molecules into simple and more degradable substances such as aldehydes, acetic acids, ketones, etc(50). As regards a effluent containing the BOD₅/COD ratio of 0.4 and higher is serve as easily biodegradable(51), it could be found from these findings that the effluent from catalytic ozonation with MgOnanocrystals treating antibiotics is biodegradable sufficient to be easily final-purified in a biological treatment plant.

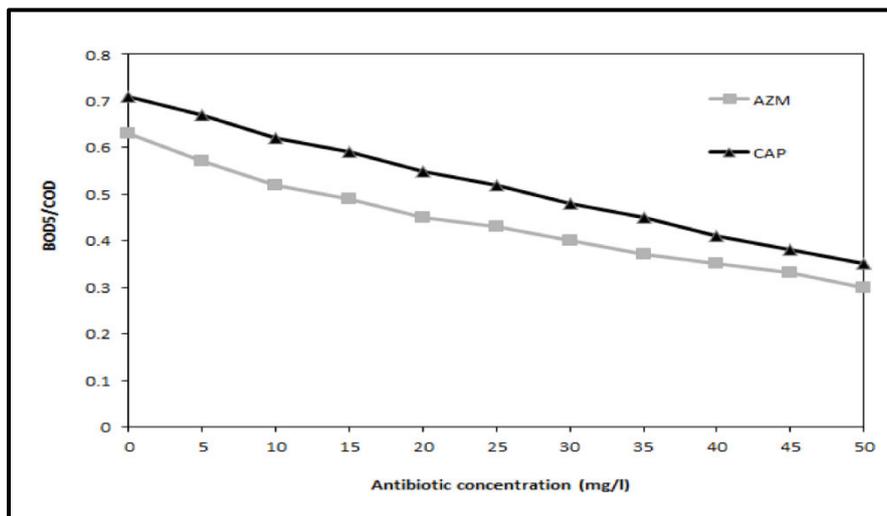


Figure- 8.Effect of catalytic ozonation on biodegradability of different concentrations of (initial pH 8.5, reaction time = 15min, MgO dosage = 6 g/L).

Conclusion

This work presents the findings of studies carried out employing MgO as a catalyst in the ozonation processes for decomposing CAP and AZM as the target antibiotic. The MgOnanocrystals have particular properties such as their destructive capability high surface area and reactivity and simplicity of their production, therefore they are promising catalysts for catalytic ozonation of antibiotic-containing effluents from both economical and technical viewpoints. MgOnanocrystals were indicated to be appropriate catalysts in the catalytic ozonation of antibiotic-containing wastewater because it significantly enhanced CAP and AZM removal and decreases the needed ozonation time compared to non-catalycozonation. The catalytic ozonation process with MgOnanocrystals can also notably enhance the biodegradability of the target antibiotic; allowing the final-purified of the effluent in a biological treatment plant.

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Corresponding Author:

SeyedEnayat Hashemi*

Email: e.hashemi@bpums.ac.ir